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Parametric Study on the Effect of Congeners on Molecular Sieve Dusting during Ethanol Dehydration

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ABSTRACT

Sieve dusting reduces the efficiency of molecular sieve adsorption during ethanol dehydration. As a result, the recoverable yield of pure ethanol is lowered. This study explored the contribution of congeners (acetone, ethyl acetate, and methanol) in molecular sieve dusting by varying the number of pressure cycles and congener concentrations during ethanol dehydration. A general two-factorial design with three levels was used to statistically test these factors. Degree of dusting was evaluated by measuring cumulative decrease in mass and change in crush strength of sieves. The number of pressure cycles and congener concentration had a positive effect on the decrease in mass of Type 3A molecular sieves and a negative effect with crush strength. There was an 11.20 %, 18.56 %, and 34.11 % change in crushing strength from 400, 800, and 1200 mg L^{-1} acetone concentration for a five-cycle dehydration run, respectively. Greatest decrease in bulk mass was found to be 0.53% (cumulative) and 0.25% (non-cumulative) for acetone and 0.60% (cumulative) and 0.31% (non-cumulative) for congener mixture. The parameters had no significant interaction towards each other; thus, the effect of the number of pressure cycle and congener concentration was additive to sieve dusting.

Key words: *acetone, congener, dehydration, ethanol, ethyl acetate, methanol, molecular sieves, pressure swing adsorption, sieve degradation, sieve dusting*

INTRODUCTION

The bioethanol industry is concerned with identifying the causes of molecular sieve dusting during dehydration process since it increases operational costs and reduces ethanol yield. In the Philippines, ethanol distilleries are commissioned to dehydrate food-grade ethanol which has higher levels of congeners fuel-grade ethanol. Congeners such as acetone, ethyl acetate and methanol are formed during fermentation whose trace amounts are left after distillation and enters the dehydration column.

Dehydration, a process of ethanol purification, can be done through extractive distillation, azeotropic distillation or pressure swing adsorption (PSA) using 3A molecular sieves. Dehydration by molecular sieves is simple and can be automated, thus reducing labor and training requirements. It is also relatively safer compared to extractive and azeotropic distillation which uses highly toxic separating agents such as benzene and cyclohexane (*Bastidas et al. 2010*). Capital investment to set-up a dehydration system by molecular sieve will costs about USD 2,376,816 (*Bastidas et al. 2010*) which is 22% lower compared to capital requirement of azeotropic distillation and 18% higher than extractive distillation.

During dehydration by molecular sieves, 95-96% (v/v) ethanol from distillation passes through a dehydration column where water molecules are retained in the sieves, resulting to a 99.95% (v/v) ethanol. The bed is regenerated by purging inert atmosphere (e.g., N_2) or by vacuum to remove water adsorbed by the sieves. In an industrial set-up, two to three dehydration columns are used to facilitate adsorption and regeneration simultaneously.

Jeong, et al. (*2012*) compared a two-bed and three-bed PSA system and found that multi-bed process has lower energy consumption and higher yield but a two-bed system can produce 99.5% ethanol from 83.1% ethanol feed. Other studies considered hybrid processes for ethanol purification such as combination of distillation with adsorption and/or vapour permeation (*Roth et al. 2013; Loyet al. 2015*).

Pressure swing adsorption is characterized by high residual loading and low operating loading. A high feed to purge pressure ratio is required to have an efficient process. Cycle time is usually short for a bed because particles respond quickly to pressure changes and column capacity is low but of high concentrations (*Green and Perry 2008*).

Ethanol is separated from water by the process of adsorption. The 3A molecular sieves are used for ethanol dehydration where highly polar water molecules (2.8 Å in diameter) (*Foust et al. 1980*) are adsorbed in the sieves while ethanol molecules (4.4 Å in diameter) will easily pass through the fixed bed.

Other studies used alternative adsorbents for ethanol-water separation such as canola meal (*Tajallipour et al. 2013; Niu et al. 2014*), natural corn cobs, natural and activated palm stone and oak (*Al-Asheh et al. 2004*). Advanced ethanol purification techniques include use of membranes (*Meireles et al. 2016*) such as hydrophilic membranes (*Kanget al. 2014*), T-type zeolite membrane modules (*Wang et al. 2017*), microbial exopolysaccharide (EPS) (*Meireles et al. 2013*) and cobalt-doped silica (*Wang and Tsuru 2011*).

PSA uses molecular sieves which are made up of inert materials with about five to ten years operational life and can be used for purification of various chemicals. However, the process also poses several disadvantages. It has less product throughput since a portion of ethanol produced is recycled for bed regeneration. It requires high power requirement to attain a vacuum pressure during bed regeneration (*Bastidas et al. 2010*). Lastly, premature bed aging occurs due to fouling of the media or mechanical destruction (*Molecular sieves technology n.d.*).

In ethanol distilleries, sieve dusting is a major factor that lowers the efficiency of molecular sieve adsorption; thus, lowering the yield of pure ethanol. Several studies have been conducted to identify the factors that causes sieve degradation.

Carbohydrates, yeasts cells, and mineral salts from upstream acid injections are some of the most common foulants during ethanol production. Since molecular sieves are alkaline, they react with mineral acids. Studies show that four pounds of sulfuric acid destroy one hundred pounds of molecular sieves (*Molecular Sieves for Alcohol Drying n.d.*).

Nolidin et al. (*2002*) identified that premature bed aging is caused by oil, olefins, diolefins, and free water. During the process, hydrocarbon contaminants decompose and polymerize on the sieve surface blocking the adsorption sites of the sieves. Free water, on the other hand, acts as a lubricant for the molecular sieve binder when the fluid is at its boiling point which further weakens the sieves' structure (*Molecular Sieves for Alcohol Drying n.d.*). Other studies identified the effect of oxygenates (e.g. methanol) (*Northrop and Sundaram 2009*), liquid water, acids and glycol concentration (*Terrigeol 2012*) to sieve degradation.

Extreme process conditions also contribute to sieve degradation. Several studies looked into the effects of liquid reflux to bed aging (*Kidnay and Parrish 2006*), shortfall in capacity and increase in pressure drop across the bed (*Nolidin 2002*), bed bumping due to depressurization, and occurrence of two-phase flow in the system (*Molecular Sieves for Alcohol Drying n.d.*).

Bioethanol distilleries explore on identifying the causes of molecular sieve degradation during dehydration using food-grade ethanol as feed. There are very few studies in the Philippines which look into the factors that cause molecular sieve degradation.

This study aimed to determine the possible contribution of congeners in the dusting of molecular sieves during ethanol dehydration. Specifically, it aimed to determine the effects of varying number of pressure cycles, varying acetone concentration, methanol-acetone-ethyl acetate ratio on type 3A molecular sieves dusting.

MATERIALS AND METHODS

Experimental Set-up

A dehydration column was designed for this study which consisted of a laboratory-scale dehydration column, heating coils, submersible pump with 2,200 L hr^{-1} capacity, a vacuum pump, condenser, feed reservoir and product-receiving vessel (**Figure 1**). This set-up was modified based from the experimental design of *Hiltz et al.* (*2008*).

Materials and Equipment

Type 3A molecular sieves from an ethanol distillery were used. Technical-grade ethanol (about 95% purity), absolute ethanol (about 99.5% purity), analytical grade isopropanol, technical grade acetone, technical grade ethyl acetate, analytical grade methanol, and used engine oil (as heating medium for heating coils) were used for the experiment.

For the analysis of ethanol and sieve samples, the laboratory apparatus used were *Shimadzu 2010* Gas Chromatograph, Kiya Seisakusho, Ltd .Hardness Tester, Mesh 10 and 16 screen, and analytical balance.

Preliminary Run

Preparation of Standard Curve. Standard curve was prepared using a 1:1:3 ratio of ethanol sample, 2% (v/v)

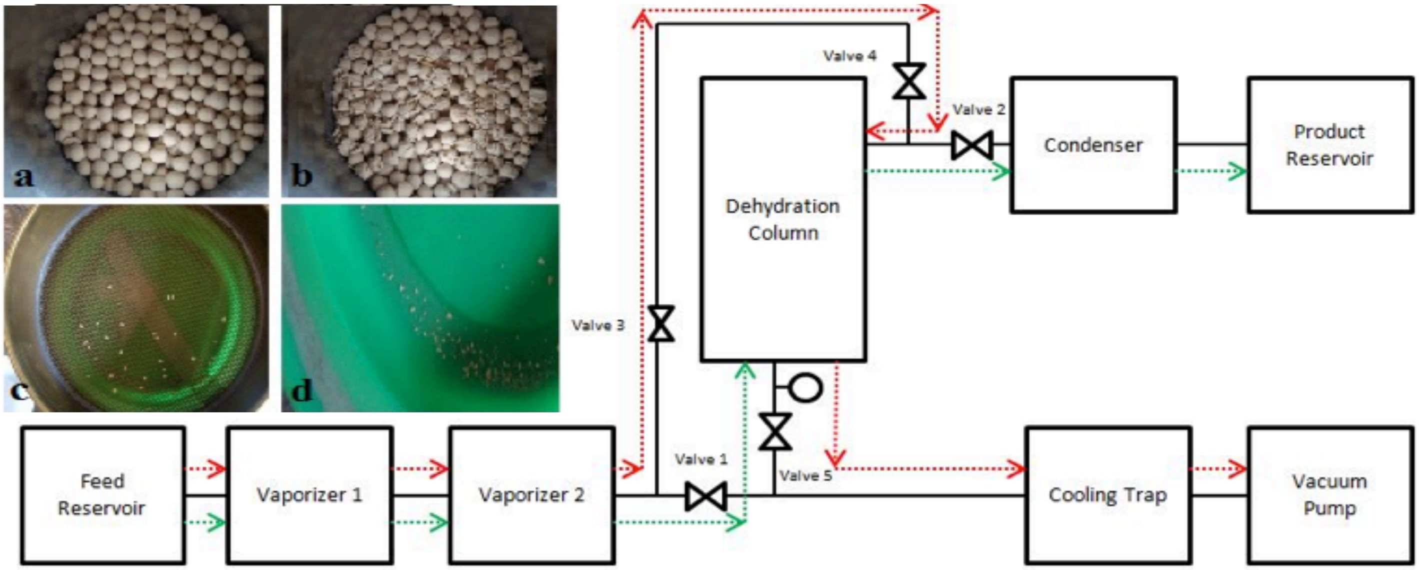

Figure 1. Schematic diagram of a adsorption (green line) and regeneration (red line) set-up: sieve degradation at top of the adsorbent bed (a) before and (b) after dehydration; (c) undersize of Mesh 10 and (d) Mesh 16 after 5 minutes of screening.

isopropanol and distilled water, respectively. The samples were analyzed using Shimadzu 2010 Gas Chromatograph.

Determination of Breakthrough Time. Breakthrough time was determined by performing a one-cycle adsorption and regeneration while sampling every 10 seconds. Samples were prepared for gas chromatography analysis by mixing the sample, isopropanol and distilled water in a ratio of 1:1:3, respectively. Ethanol concentration for each sample was determined using the standard curve equation. The concentrations were then plotted to determine the breakthrough time.

General Experimental Procedure

Feed Preparation. For acetone solution, 400, 800 and 1200 ppm of acetone solutions using technical grade ethanol as solvent were prepared. For mixture of congeners, stock solution of congener solution with volume ratio of 1:0.75:0.01 (v/v/v) methanol to ethyl acetate to acetone was prepared. From the stock solution, 1%, 2% and 3% congener-ethanol solutions were prepared for feed. Technical grade ethanol was used as control. Absolute ethanol (analytical grade) was used as feed during regeneration.

Molecular Sieve Preparation. Fresh batch of Type 3A molecular sieves was screened and reactivated by drying at 150 ºC for 1 hr. Six hundred thirty-five grams of prepared sieves was randomly packed in the dehydration column.

Dehydration Cycle. The feed at ambient temperature in the reservoir was pumped through a submersible pump to the heater and vaporizer. Feed was introduced to the column with a feed flowrate of 2.33 L min^{-1}. Adsorption pressure was at 1.14 to 1.27 atm while regeneration pressure was maintained at 26 in Hg (vacuum pressure). The hot gas product of adsorption was condensed to its final liquid form into a receiving vessel (**Figure 1**). Temperature of engine oil (heating medium) for the two vaporizers were maintained at 140 to 160 ºC and 170 to 190 ºC, respectively. Adsorption and regeneration was done for four minutes and one second each based from the pre-determined breakthrough time. Five, ten and fifteen cycles were performed with two trials for each parameter tested.

Molecular Sieve Dusting Determination

Determination of Bulk Change in Mass. Molecular sieves were carefully unloaded and were spread evenly in an aluminum pan after every cycle. The sieves were dried for one hour at 150°C. During drying, the sieves were slightlyshaken every 10 min to facilitate efficient heating. The sieves were then screened through Mesh 10 and Mesh 16 to separate degraded sieves. After which, the sieves were cooled for 15 min in a closed container.

Determination of Crushing Strength. Five molecular sieves were randomly sampled and were subjected to the Hardness Tester (Kiya Sei Sakusho, LTD).

Statistical Analysis

A general two-factorial design with three levels using 2-WAY Analysis of Variance was used for statistical analysis of data. Microsoft Excel TM was used for statistical calculations.

RESULTS AND DISCUSSION

Determination of breakthrough time

The breakthrough time is the time at which first trace of water is detected in the product stream due to bed saturation. Graphically, breakthrough time is the point where c/cf or the final water concentration to feed water concentration ratio is equal to 0.1 (*McCabe et al. 1993*). Interpolating from the data gathered the breakthrough time was found to be 241s or 4 min and 1s.

The regeneration time was assumed to be equal to adsorption time based from the ethanol dehydration process of Green Futures Innovation Inc. (GFII). Thus, the regeneration time used was 4 min and 1s. A typical cycle time for pressure swing adsorption ranges from 5 to 30 min (*Hiltz et al. 2008*). The total cycle time used was 8 min and 2 s which was within the typical cycle time for PSA. A study by *Chen* (*2014*) recorded a breakthrough time of 20 min and reached saturation at 60 to 100 min for a 200-L feed volume.

Effect of acetone concentration

The concentration of acetone was based from the study conducted by *Jung et al.* (*2010*). The chosen alcoholic beverage with the highest acetone concentration was a home-made plum spirit from Salaj, with 40 mg L^{-1} acetone content. The concentration was multiplied by a factor of 10, 20, and 30 to magnify the effect of acetone concentration to the dusting of sieves.

Cumulative decrease in mass was measured to evaluate the degree of dusting since the sieves were reused every five cycles. Same batch of sieves were used for each acetone concentration.

Increase in acetone concentration resulted into a greater degree of dusting (**Figure 2a**). From the screening process, only very few dusts were observed. It was because some dusts formed during dehydration came out with the product or were carried away during depressurization. This was evident when dust particles were observed at the coldtrap and at the pipeline going to the condenser.

The non-cumulative plot was used to determine if increasing the number of pressure cycles would result to sieves' production of more dusts. This would show that the sieves left from the previous cycles weakened.

It was observed that the amount of degraded sieves per five cycles relatively increased with the acetone concentration (**Figure 2b**). Thus, the sieves produced more dusts and relatively weakened. Based on statistical analysis, acetone concentration had a significant effect on molecular sieve dusting.

After every five cycles at each acetone concentration, five randomly selected sieve samples were tested for their crush strength using a hardness tester (Kiya Seisakusho, Ltd.). For the crush strength test, the average crush strength of the sieves decreased when acetone concentration was increased (**Figure 2c**).

The feed without acetone served as the control variable. Comparing the average crush strength of the sieves from the control, there were 11.20 %, 18.56 %, and 34.11 % difference from 400, 800, and 1200 mg L^{-1}, respectively, for a five-cycle dehydration run. The increasing the acetone concentration lessened the strength of molecular sieves (**Figure 2c**).

Acetone is a slightly acidic substance. The low pH solution increases the removal of silicon from the sieves, more than the removal of aluminum when it comes in contact with molecular sieves. Also, proton exchange occurs resulting in hydronium ion formation and this competes with the ion exchange process when zeolites come in contact with acidic solutions (*Sherman 1983*).

Acetone has a molecular diameter of 3.08 A. This suggests that during dehydration, acetone molecules will not be adsorbed by 3A molecular sieves; instead it will slide through the bed. The effect of acetone to molecular sieves is on the outer portion of the beads and to its binder which causes dusting and brittleness.

The outliers from the data obtained are also evident because of the hydrophilicity of the sieve samples. Molecular sieves are hygroscopic material. Although the samples have been regenerated, internal structures were greatly affected once they have been exposed to air for some time. The fluctuations on the graph show that gas flow distribution during dehydration is non-uniform; thus, some sieves may not be as damaged as the other sieve samples during each cycle (**Figure 2**). This in turn resulted in a higher or lower crushing strength compared to other samples. Statistically, acetone concentration had a significant effect on the crush strength of the sieves at 95% confidence interval.

Effect of congener concentration

The ratio of concentration of congeners used was based from home-made plum from Salaj. The congeners used were ethyl acetate, acetone, and methanol. Plum spirit (Salaj) has a composition of 52% (v/v) ethanol, 3710 mg L^{-1} methanol, 40 mg L^{-1} acetone (*Jung, et al. 2010*) and 277.39 mg L^{-1}

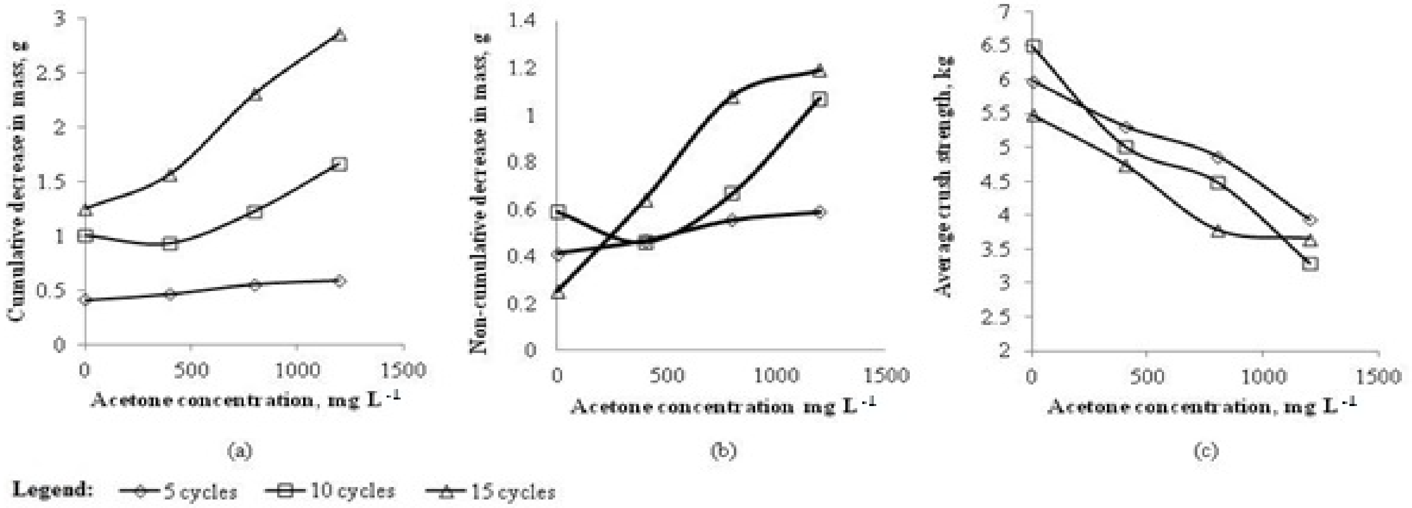

Figure 2. Effect of acetone concentration to sieve dusting on (a) cumulative decrease (b) non-cumulative decrease and on (c) the average crush strength of 5 randomly selected sieves at 5, 10, and 15 cycles.

ethylacetate (*Beceau and Nicalau 2009*). From these values, the concentration of each congener was multiplied by a factor of 10, 20, and 30, while retaining the ratio of the congeners.

Increase in congener concentration resulted into an increase in sieve degradation (**Figure 3a**). On the other hand, a non-cumulative plot (**Figure 3b**) shows that there is an increase in dusts formed when the number of pressure cycles was increased. From the plot, it can be observed that there is an increase in dusts formation at increasing congener concentration (**Figure 3b**). Statistical analysis shows that congener concentration had a significant effect on the degree of molecular sieve dusting.

The crush strength of the sieves samples decreased when congener concentration was increased (**Figure 3c**). However, during the first five cycles, the crush strength of the sieves at 3 % (v/v) congener concentration significantly increased. This was due to a representative sieve wherein its crush strength deviated from the crush strength data of the other four randomly selected samples. This can be attributed to the uneven gas flow distribution during the dehydration process, which resulted in non-uniformity in the properties of the sieves after each run.

Ion exchange caused complete loss of crystallinity of Na+A, thus weakening the structure of the sieves in methanol solutions (*Sherman 1983*). Liquid substances were also observed at the topmost and bottom most portion of the bed after dehydration. This shows that the adsorbent has come in contact with liquid substance, which caused further dusting of the sieves.

Free water during adsorption attacks the binder and material of the sieve. Also, adsorption rate of liquid in a column is slower by a factor of 10, thus contact time must be prolonged. This reduces the working capacity of the sieves and results in early breakthrough or early bed saturation (*Molecular Sieves for Alcohol Drying n.d.*). Statistically, congener concentration had no significant effect on the crush strength of molecular sieves.

Comparing the decrease in mass using acetone and using a mixture of acetone, methanol, and ethyl acetate, it was observed that the highest amount of decrease for using acetone only was found to be 3.38 g and 1.59 g for cumulative and non-cumulative mass. On the other hand, using the mixture of congener, the highest decrease in mass was found to be 3.79 g and 1.99 g for cumulative and non-cumulative mass. This showed that the mixture of congener mixed with ethanol had a greater effect on dust formation compared when only acetone was present as congener in ethanol.

Ethyl acetate, acetone, and methanol molecules were larger than 3 Å and were not adsorbed by the molecular sieves. Instead, they slipped through the bed and reacted with the outer layer of the beads.

Effect of number of pressure cycles

There was a direct relationship between the number of pressure cycles and the mass of degraded sieves (**Figure 4a** and **Figure 4d**). Cumulative mass of degraded sieves was used as a measuring parameter since the same batch of sieveswas used for 5, 10, and 15 cycles at each concentration. It was assumed that the amount of sieves degraded accumulates as the number of pressure cycles was increased. A non-cumulative plot (**Figure 4b** and **Figure 4e**) was made to identify the specific mass of degraded sieves when pressure cycle was increased by five cycles. From the non-

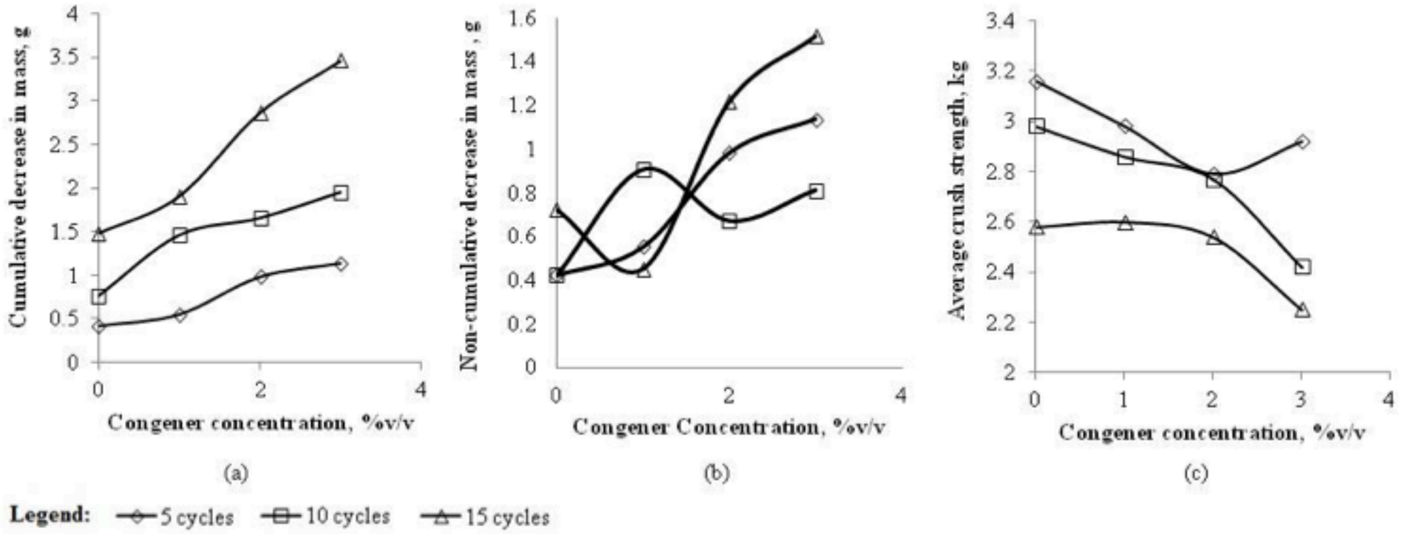

Figure 3. Effect of congener concentration on sieve dusting on (a) cumulative decrease and (b) non-cumulative decrease in mass and on (c) the average crush strength of 5 randomly selected sieves at 5, 10, and 15 pressure cycles.

cumulative plot, it can be observed that the non-cumulative mass of sieves increased as the pressure cycle is increased.

The *CECA* (*2011*) stated that switching the process from adsorption to regeneration caused movement in the column varying pressure in the column. During the experiment proper, "shaking" was observed every time the process was changed from adsorption to regeneration. This caused the sieves to hit the sides of the column and strike against each other. Also, the sieves in the column were randomly picked; thus, pressure changes in the column caused attrition of sieves to each other during bed movement, which then caused dusting or disintegration of sieves.

Extrapolating from the data gathered at each acetone concentration from 15 cycles to 300 cycles, the cumulativedecrease in mass (% decrease in mass) were the following: 25.25 g (3.98%), 32.89 g (5.10%), 51.96 g (8.18%) and 67.24 g (10.59%) for control, 400, 800, and 1200 mg L^{-1} acetone-ethanol solution, respectively.

The cumulative decrease in mass (% decrease in mass) were the following: 31.63 g (4.98 %), 40.60 g (6.39%), 56.50 g (8.90%), and 69.61 g (10.96%) g for control, 1%, 2%, and 3% (v/v) congener-ethanol solution, respectively. Statistical analysis showed that the number of pressure cycles had a significant effect on dust formation of the sieves.

Extrapolating from the data gathered at each congener concentration from 15 cycles to 300 cycles, the cumulative % decrease in mass were the following: 31.63 g (4.98%), 40.60g (6.39%), 56.50 g (8.90%) and 69.61g (10.96%) for control, 1%, 2% and 3% (v/v) congener-ethanol solution, respectively. Statistical analysis showed that the number of pressure cycles had a significant effect on the dust formation of the sieves.

The increasing number of pressure cycle affects average crush strength of the sieves (**Figures 4c** and **Figure 4f**). As the number of pressure cycle was increased, the average crush strength of the sieves generally decreased. The adsorbent had undergone some physical changes. It can be observed that there was an irregular trend in the crush strength of the samples fromthe blank (**Figure 4c**). There was a sudden increase in crush strength to a sieve sample during the tenth cycle.

It can be seen that there was a similar decreasing trend for molecular sieve crush strength when the concentration of congener was increased (**Figure 4f**). There was a drastic change at 3% (v/v) congener compared to the 1% and 2% congener concentration in the feed. From the slope of the line, the 3% (v/v) line had the lowest slope among the four series. Statistical analysis shows that the number of pressure cycle had no significant effect to the crush strength of the beads.

From the statistical analysis, it was also found out that the interaction between the number of pressure cycle and and the congener concentration and between the number of pressure cycle and the acetone concentration used had no significant effect to dusting.

The number of pressure cycles, the concentration of congener, and acetone used affect sieve dusting but these variables were not necessary to have interaction effects. This shows that simultaneous effect of the parameters produced an additive effect to the extent of dusting of the sieves.

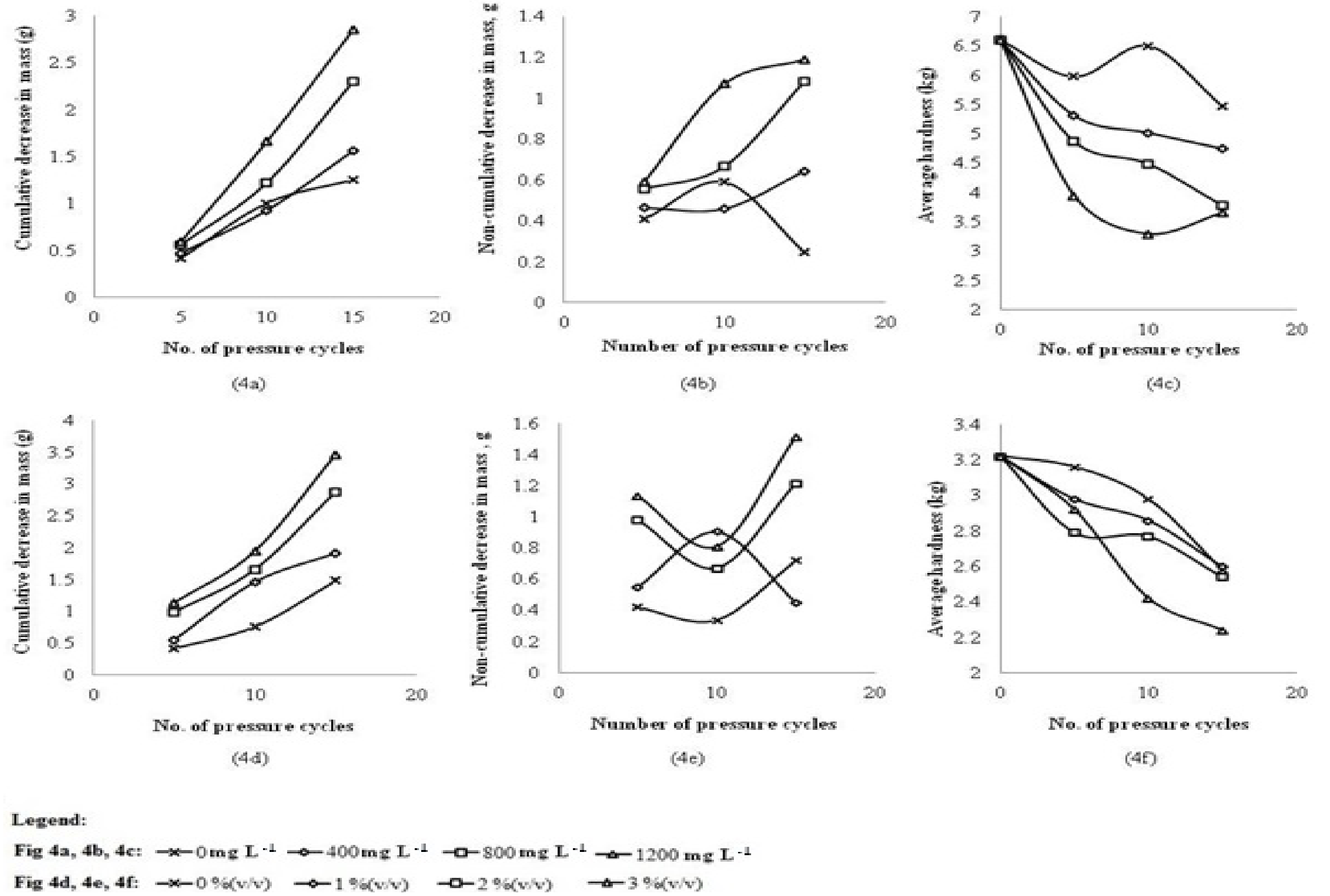

Figure 4. Effect of pressure cycle to the (a) cumulative and (b) non-cumulative mass of degraded sieves and (c) average crush strength at different acetone concentration, to the (d) cumulative and (e) non-cumulative mass of degraded sieves and (f) average crush strength at different congener concentration.

CONCLUSION AND RECOMMENDATIONS

Type 3A molecular sieves were tested for its extent of dusting using different parameters namely, number of pressure cycles, varying acetone concentration, and varying congener concentration. The breakthrough time was found to be at 4 min and 1s. It was found out that there was a direct relationship between the number of pressure cycles and concentration of acetone and congeners to the degree of sieve dusting. There was an inverse relationship between the number of pressure cycles and concentration of acetone, and congeners to the crush strength of the sieves.

It is recommended that further study be conducted to analyze the internal structure of the molecular sieves before and after ethanol dehydration process. The number of pressure cycles should also be increased in order to further evaluate sieve dusting. It is recommended to explore other congeners involved during the production of food grade ethanol. Sieve manufacture involves different binders which can influence sieve crush strength. Different binders can be tested in order to investigate its inherent effect on sieve dust formation.

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